# NOVEL ACTIVE TRANSIENT COOLING SYSTEMS

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**FINAL TECHNICAL REPORT**

## Executive Summary

Under this grant, we have conducted detailed studies of magnetocaloric nanomaterials for solid state cooling applications. Such materials are of great current interest, in fact, the current AFOSR MURI Topic #20 is exclusively devoted to solid state cooling. Our work on synthesis, characterization and property evaluation of magnetocaloric materials is summarized. Magnetic refrigeration systems offer good potential to reduce (1) global energy consumption and (2) use of ozone-depleting compounds, greenhouse cases and hazardous chemicals. The experimental investigation of magnetocaloric effects and structural properties of $Fe_{80-x}Gd_xCr_8B_{12}$ (x = 0, 5, 8, 15) alloys has therefore been studied. $Fe_{80}Cr_8B_{12}$ alloys exhibit good magnetocaloric properties near room temperature. Gd, which is well-known to exhibit good magnetocaloric effects in room temperature, was alloyed in Fe-Cr-B base alloys. The increase of Gd additions displaces the Curie temperature of the alloy to higher temperatures without significant depreciation of $\left|\Delta S_M^{pk}\right|$. It is also shown that a phenomenological model which describes the magnetic entropy change is applicable to these alloys.

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14. ABSTRACT
**Under this grant, researcher has conducted detailed studies of magnetocaloric nanomaterials for solid state cooling applications. Such materials are of great current interest in solid state cooling. Present work on synthesis, characterization and property evaluation of magnetocaloric materials is summarized. Magnetic refrigeration systems offer good potential to reduce (1) global energy consumption and (2) use of ozone-depleting compounds, greenhouse gases and hazardous chemicals. The experimental investigation of magnetocaloric effects and structural properties of Fe80-xGdxCr8B12 (x = 0, 5, 8, 15) alloys has therefore been studied. Fe80Cr8B12 alloys exhibit good magnetocaloric properties near room temperature. Gd, which is well-known to exhibit good magnetocaloric effects in room temperature, was alloyed in Fe-Cr-B base alloys. The increase of Gd additions displaces the Curie temperature of the alloy to higher temperatures without significant depreciation of entropy change. It is also shown that a phenomenological model which describes the magnetic entropy change is applicable to these alloys.**

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# Introduction

Energy efficient cooling technology is extremely important in today's society considering the great need for energy conservation and the urgent need to mitigate global warming. Near room temperature magnetic refrigeration is an emerging cooling technology which has several advantages compared to conventional gas-compression technology. It utilizes the magnetocaloric effect (MCE) in which heating and cooling of a magnetocaloric material (MCM) is induced by a varying external magnetic field. We briefly present the basic principles and major advances in the developments of MCM.

### 1.1 General introduction

The magnetocaloric effect, i.e., the temperature change of a magnetic material due to the application of an external magnetic field, is the cornerstone of magnetic cooling. This phenomenon was first demonstrated by Warburg in 1881, using pure iron metal, which displayed a cooling effect of 0.5 – 2 K per tesla. Since then, many materials with large MCE have been discovered, providing better understanding of this effect.

In a magnetic material, entropy is a combination of contributions from the lattice as well as from electronic and magnetic spins. Upon an adiabatic application of an external magnetic field, the magnetic spins align parallel to the field, which causes the magnetic part of the entropy to decrease. The lattice entropy consequently increases, leading to a temperature rise in the material. This heat is removed from the material to its surroundings by a heat-transfer medium (depending on the operating temperature, the heat-transfer medium may be water or air, and for very low temperatures, helium). When the field is removed under adiabatical conditions, the magnetic material cools down to below ambient temperature due to an increase in disorder of the magnetic spins, this result in lower lattice entropy. This describes the normal MCE (figure 1) while the inverse effect would result in a lower temperature with an applied magnetic field.

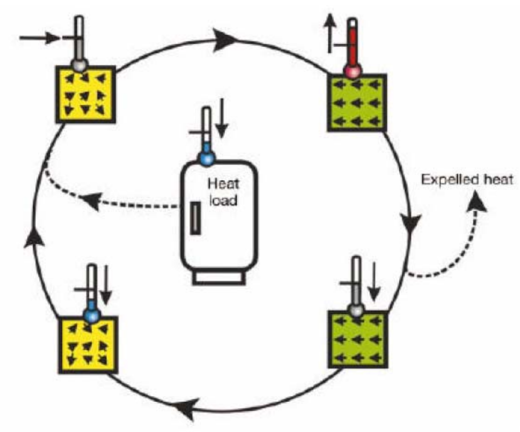


Figure 1 Schematic representation of a magnetic refrigeration cycle in which heat is transported from the heat load to its surroundings [2].

Magnetic refrigeration is based on the MCE. Major advances occurred in the late 1920s when cooling through adiabatic demagnetization was independently suggested by Debye and Giauque. The process was demonstrated to reach temperatures as low as 0.25 K in 1933. Since then, interest in the utilization of MCE concentrated on cooling at low temperatures until a proof-of-principle near room temperature (RT) magnetic refrigerator (MR) was unveiled, on February 20, 1997. It was demonstrated using Gd, which was exposed to magnetic fields of 50 kOe, that magnetic refrigeration is capable of achieving a record cooling power of 600 W, coefficient of cooling power (COP) of 15 (typical gas compression refrigerators have COPs between 2 and 6), maximum Carnot efficiency of 60% and maximum temperature span of 38 ºC . MR, as an alternative to conventional gas compression refrigeration technologies, has advantages such as operating cost savings (it eliminates the most inefficient part of the refrigerator – the compressor) and environmental friendliness (no hazardous/ozone depleting gases are involved). However, this technique was limited by the lack of good candidate materials with large MCE for low magnetic fields.

The announcement of giant MCE (GMCE) in $Gd_5(Si_2Ge_2)$ on June 9, 1997 by Pecharsky and Gschneidner was another breakthrough in magnetic cooling technology. There were two major developments which resulted in a flurry of research activities in new magnetic refrigerants and MR designs (figure 1.2) [18]. By the end of 2006, more than twenty laboratory-scale magnetic cooling units had been built and tested.

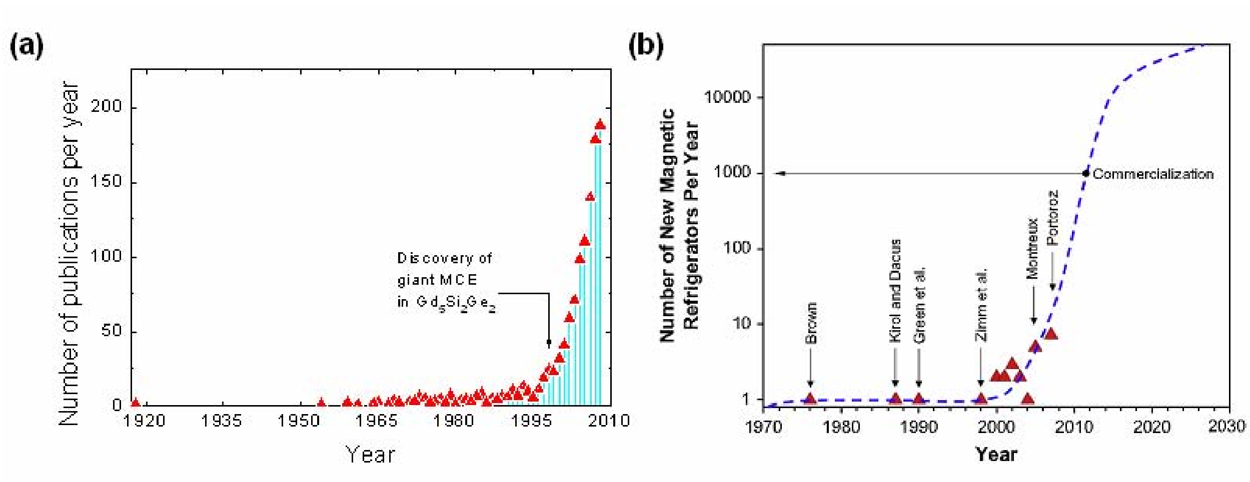


Figure 2 The annual number of publications on magnetic cooling: (a) research papers containing the words "magnetocaloric", "magnetic entropy" or "magnetic refrigeration" in the title (the bibliographic search is dated up to December 2008) and (b) reported near room-temperature magnetic refrigerators.

Among the factors (economical production and processing methods of magnetic refrigerants into media suitable for magnetic cooling, improvements in the thermodynamic efficiency, mechanical design of the MR and the equipment to produce the magnetic fields) needed to make a successful operating MR, the MCM is of principal importance. A new MCM with promising MCE must be tested under realistic operating conditions in order to evaluate its applications in practical MR.

Fe-based amorphous soft magnetic alloys, which are less than 5% of the cost of Gd-based alloys, were recently intensively studied for MCE applications. They were discovered to exhibit reasonable $\Delta S_M^{pk}$ and large refrigerant capacity (RC) values for high temperature applications. $Fe_{80}Cr_8B_{12}$ amorphous ribbons were recently reported to exhibit reasonable MCE near room-temperature (RT) ($\Delta S_M^{pk}$ =0.93 J kg$^{-1}$ K$^{-1}$ for fields up to 1.5 T with $T_C$ at 328 K). An universal curve can be constructed, the practical applications of the universal curve include: (1) a simple screening procedure of the material performance, (2) provides a method for making extrapolations to temperatures or magnetic fields which are not readily accessible, this simplifies the identification of novel MCM.

**Significance**

MCE is the vital element of near room-temperature magnetic cooling, which is poised for commercialization in the future and is an energy efficient and environmentally friendly alternative to gas compression refrigeration technology. In addition, MCE is intrinsic to every magnetic solid and is of fundamental importance; it is related to diverse topics such as spin dynamics and physical properties such as thermal conductivity. Understanding and controlling MCE is a challenging task. Understanding the influence of chemical composition and microstructure on physical properties would help to develop a material with an attractive combination of magnetic and thermal properties.

**Experimental Procedures**

The samples were prepared by arc melting and melt spinning from elemental precursors. The resultant ribbons were studied by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The field dependence of magnetization was measured by a Lakeshore 7404 vibrating sample magnetometer (VSM) using a maximum applied field of 1.1 T for constant temperatures in the range of 250 – 525 K with increments of 10 K.

**RESULTS**

**Structural Analysis**

The amorphous nature of the samples are studied by varying the ribbon thickness and the composition of the alloys (figure 3). The large quench rate ($10^6$ K/s) required in order to bypass crystallization in the melt spinning technique, limits the ribbon thickness for amorphous alloys to ~ 50 μm. Hence, Gd0 ribbons of varying ribbon thickness were intially used to study if they were amorphous. Several well-resolved diffraction peaks are observed for Gd0 ribbons (thickness > 50 μm) with minor oxidation. When Gd0 ribbons are reduced to less than 20 μm, the presence of several phases are significantly reduced. However a small crystalline peak corresponding to $Cr_5B_3$ phase could be observed, suggesting that the alloy is not fully amorphous. Broad peaks with low relatively low intensities were observed for the as-spun Gd5 and Gd8 alloys. For Gd15, peaks corresponding to $Cr_5B_3$ and $GdB_6$ phases could be observed, suggesting that the alloy is not a completely amorphous.

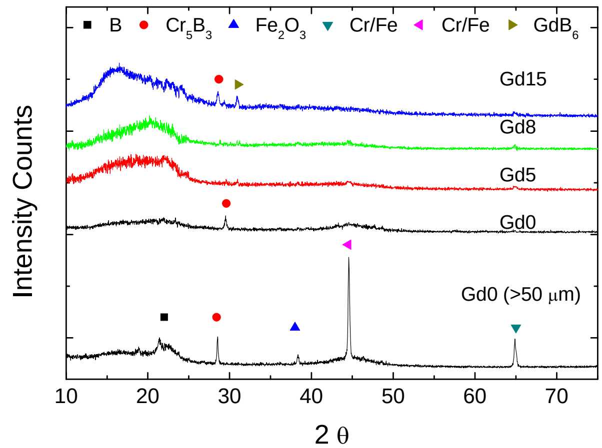


Figure 3 XRD patterns for as-spun $Fe_{80-x}Gd_xCr_8B_{12}$ ribbons.

## 4.2 Property evaluation

### 4.2.1 Compositional dependence of MCE

A representative example of the magnetization curves are shown for the Gd5 alloy are plotted in figure 4. The magnetic entropy change values are calculated from the M(H) data sets.

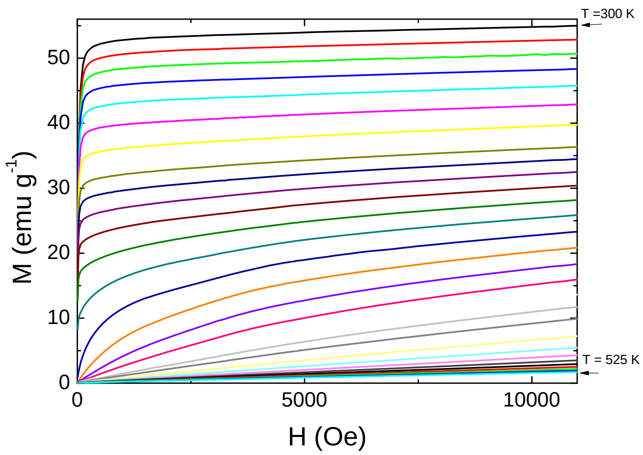


Figure 4 Experimental VSM magnetization curves for Gd5 alloy.

The temperature dependence of the magnetic entropy change of the studied alloys is presented in figure 5

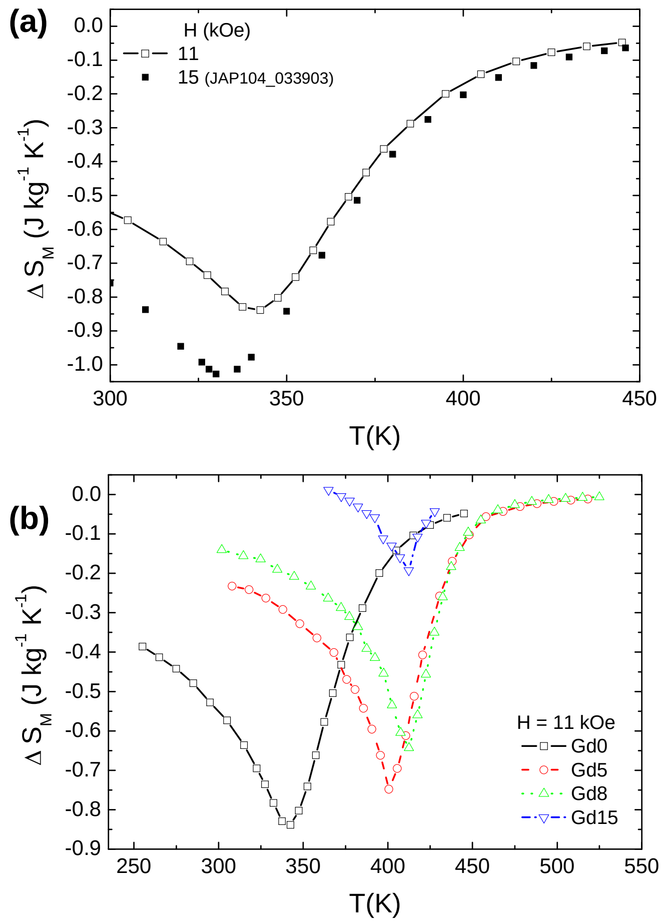


Figure 5 Experimental values of the magnetic entropy change calculated from VSM magnetization data for: (a) Gd0 (comparison with literature values) and (b) as-spun $Fe_{80-x}Gd_xCr_8B_{12}$ ribbons. Lines are a guide for the eyes

The peak magnetic entropy change at a maximum applied magnetic field of 11 kOe for Gd0, Gd5 and Gd8 alloys are 0.84, 0.75 and 0.66 J/kg•K respectively. The temperature of the peak entropy change is displaced to higher temperatures with increasing Gd content. There is not much large difference in $\Delta S_M^{pk}$ for higher Gd content (figure 6).

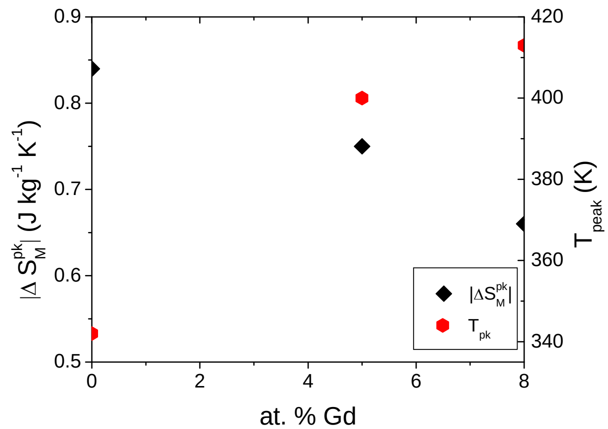


Figure 6 Compositional dependence of $\Delta S_M^{pk}$ and temperature of the peak magnetic entropy change of the as-spun ribbons.

The slight decrease in $\Delta S_M^{pk}$ observed in Gd8 as compared to Gd5 could be due to the decrease in magnetization. The drop in magnetization could be due to exchange interactions between Fe, Gd and B (Cr is reported to be nonmagnetic in Fe-Cr-Gd alloys).

### 4.2.2 Field dependence of MCE

The temperature dependence of the local experimental values of exponent *n* controlling the field dependence of the magnetic entropy change when different magnetic fields are applied is shown in figure 7 The general behavior comprises (a) a value of *n* close to 1 for temperatures below the transition temperature, (b) a smooth decrease of *n* down to values close to 0.73 at $T_{peak}$ ($T_C$) and (c) a subsequent increase to $n$ = 2 in the paramagnetic region, showing good agreement with the experimental data for other soft magnetic alloys studied.

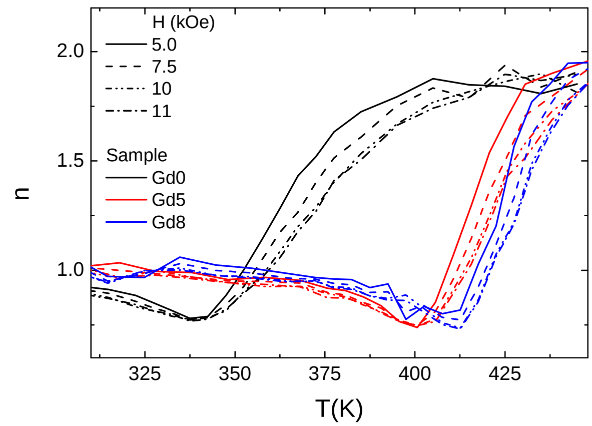


Figure 7 Temperature dependence of the exponent characterizing the field dependence of $\Delta S_M$ for $Fe_{80-x}Gd_xCr_8B_{12}$ alloys.

### 4.2.3 Universal curve behavior

Gd5 was observed to follow the universal curve when measured at different maximum applied fields (figure 8). This shows that the universal curve model is applicable to the alloy at different applied magnetic fields.

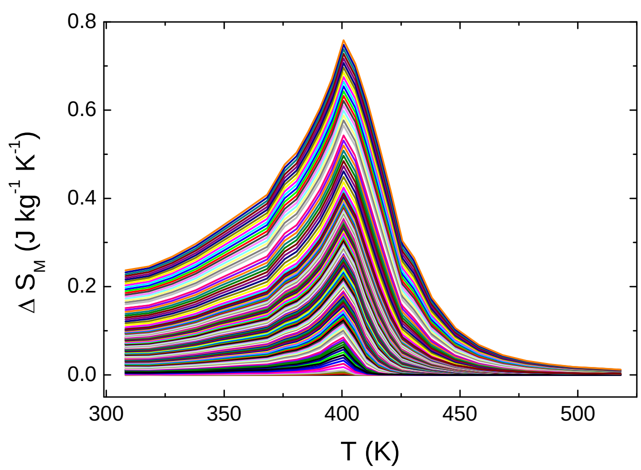


Figure 8 Temperature dependence of magnetic entropy change curves of Gd5 for maximum applied fields ranging from 2.5 up to 11 kOe (132 curves)

Comparison of the MCE of the studied alloys with other MCM, tabulated in table 1 (for 11 kOe and 15 kOe) and table 2 (for 11 kOe and 50 kOe) could be easily obtained from the field dependence. It should be noted that the Gd0 alloys exhibit similar $\Delta S_M^{pk}$ values as those reported in the literature. Importantly, it should be noted that the RC of Gd5 and Gd8 alloys compare favorably to the well-known GMCE material (GdSiGe-type alloys).

| Sample ID | $T_C$ (K) | $\left|\Delta S_M^{pk}\right| (Jkg^{-1}K^{-1})$ | | $\left|RC\right| (Jkg^{-1})$ | |
|---|---|---|---|---|---|
| | | H = 11 kOe | H = 15 kOe | H = 11 kOe | H = 15 kOe |
| Gd0 | 342 | 0.84 | 1.09 | 90.77 | 131 |
| Gd5 | 400 | 0.75 | 0.95 | 42.92 | 73 |
| Gd8 | 413 | 0.66 | 0.85 | 32.16 | 45 |
| Gd15 | 412 | 0.19 | 0.23 | 4.5 | 7 |
| Amorphous $Fe_{80}Cr_8B_{12}$ | 328 | - | 1.07 | - | 134 |
| Amorphous $Fe_{83}Zr_6B_{10}Cu_1$ | 398 | - | 1.40 | - | 137 |
| Amorphous $Fe_{78}Co_5Zr_6B_{10}Cu_1$ | 488 | - | 1.60 | - | 120 |
| Amorphous $Fe_{71}Mo_8Cu_1B_{20}$ | 386 | - | 0.92 | - | 54 |

Table 1 Comparison of experimental values of peak temperature and peak entropy change measured in $Fe_{80-x}Gd_xCr_8B_{12}$ ribbons and published soft magnetic alloys.

| Sample ID | $T_C$ (K) | $\left\|\Delta S_M^{pk}\right\|(Jkg^{-1}K^{-1})$ | | $\left\|RC\right\|(Jkg^{-1})$ | |
|---|---|---|---|---|---|
| | | H = 11 kOe | H = 50 kOe | H = 11 kOe | H = 50 kOe |
| Gd0 | 342 | 0.84 | 2.8 | 90.77 | 545 |
| Gd5 | 400 | 0.75 | 2.3 | 42.92 | 294 |
| Gd8 | 413 | 0.66 | 2.2 | 32.16 | 171 |
| Gd15 | 412 | 0.19 | 0.6 | 4.5 | 25 |
| Gd | 294 | ~ 2.8 | 10.2 | - | 410 |
| Amorphous $(Fe_{90}Co_5Cr_5)_{91}Zr_7B_2$ | 230 | - | 2.9 | - | 320 |
| Amorphous $(Fe_{85}Co_5Cr_{15})_{91}Zr_7B_2$ | 320 | - | 2.8 | - | 240 |
| $Gd_5Si_2Ge_2$ | 275 | ~ 4.3 | 19 | - | 200 |
| $Gd_5Si_2Ge_{1.9}Fe_{0.1}$ | 305 | - | 7 | - | 235 |

Table 2 Comparison of experimental values of peak temperature and peak entropy change measured in $Fe_{80-x}Gd_xCr_8B_{12}$ ribbons and literature.

## Conclusions

In conclusion, the magnetocaloric response of $Fe_{80-x}Gd_xCr_8B_{12}$ (x = 0, 5, 8 and 15) alloys was studied. Gd addition decreases the peak entropy change slightly and displaces $T_C$ to higher temperatures. The RC values of $Fe_{80-x}Gd_xCr_8B_{12}$ alloys comparable favorably to those in GMCE materials and also the alloys are much cheaper than the rare-earth-based MCM. The universal curve models are applicable to the studied alloys. The exponent *n* controlling the field dependence of the magnetic entropy change enables easier MCE extrapolations of the alloys at different magnetic fields.

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## **APPENDIX 1:** Recent recognition of PI's work

- **Research Advisory Committee**, Vels University, India (2009).
- **Research Advisory Committee**, Asthagiri Foundation (affiliated to Madras University) (2009).
- **Guest Professor**, South China University of Technology, China (2009).
- **Visiting Professor**, Center for Future Energy Systems, RPI (USA) (2008).
- **Editorial Board,** Advances in Materials Science and Engineering (since 2008).

- **Secretary, Magnetic Materials Committee**, TMS (USA) (since 2009).
    - **Advisory Committee,** International Conference on Nanoscience and Nanotechnology, India (2010).
    - **Invited Talk**, Functional oxide nanostructures and heterostructures, MRS Meeting, San Francisco, USA (2010).
    - **Symposium Organizer**, Domain Microstructures and Mechanisms for Advanced Properties in Phase Transforming Materials, Materials Science &Technology Conference, USA (2009).
    - **International Advisory Committee and Invited Speaker**, Nanomaterials Conference, Cochin University of Science and Technology (2009).
    - **Plenary Presentation**, 1$^{st}$ International Forum of the 94$^{th}$ Annual Meeting of the Japanese Society of Gastroentrology, Fukuoka, Japan, May 9 (2008).
    - **Invited Talk and Session Chair**, Biomaterials Symposium, MS&T Meeting, Pittsburgh, USA (2008).
    - **Invited Talk and Session Chair**, Nanomaterials Symposium, TMS Annual Meeting, New Orleans, USA (2008).
    - **Session Chair**, Biological Materials Science Symposium, TMS Annual Meeting, New Orleans, USA (2008).
    - **Invited Speaker**, Workshop on Probabilistic and Resilient Architectures for Nanoscale Computing, Rice University, USA (2008).